

## SOLUTE GENERATION AND TRANSFER FROM A CHEMICALLY REACTIVE ALPINE GLACIAL–PROGLACIAL SYSTEM

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### ABSTRACT

The environs of the Glacier de Tsanfleuron, Switzerland, was used as a study site to investigate the controls on the relative efficiency of solute generation and removal from glacial and proglacial environments. Here, a 1500 m wide glacier forefield consists of a karstic limestone plateau flanked to the north by a till-floored valley. Bedrocks and glacial debris are composed of chemically reactive pure and impure Mesozoic and Tertiary limestones with accessory pyrite. Spot sampling of ice, snow and meltwaters in the late melt season was supplemented by systematic measurements of the main meltstream, including during periods of rainfall, and simple laboratory leaching and weathering experiments.

Isotopic parameters were used to investigate water sources. Most meltwater and glacier ice samples lay close to a meteoric water line ( $\delta D = 8.3 \delta^{18}O + 14$ ) defined by waters from small tributary streams. Heavy isotopic excursions of bulk meltwater chemistry were caused by rainfall events, recovering within days to a  $\delta^{18}O$  baseline around  $-12$  permil. No regular diurnal variations in  $\delta^{18}O$  were apparent.

The atmosphere is the source of  $Cl^-$  and most  $Na^+$ , but the bulk of other solutes are generated in the environment. Ion loads of up to  $1 \text{ meq l}^{-1}$  are rapidly attained by calcite dissolution. Over periods of weeks to months pyrite oxidation generates sulphate and acidity that drives further calcite dissolution. Low water–rock ratio weathering environments have characteristically high  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$ , and ratios of these species to calcium. The characteristic cation ratios are influenced by non-congruent calcite dissolution. The ratio of sulphate to other species is highest where water–rock contact times are highest, although this relationship is complicated by spatial variations in pyrite abundance.

Meltstream time series illustrate that 90 per cent of daily ion yields in fine weather are concentrated in the 12 h time period of higher discharge. Ion yields increase downstream mainly by a combination of dissolution of calcareous suspended sediment and input from tributaries and seepage from the till banks. Rainstorms lead to increased solute concentrations and resulting hourly fluxes can match daily fine weather ion fluxes. Excess nitrate appears to be largely sourced from the proglacial surface. The capacity of the proglacial environment for yielding significant subsurface water as a result of the storm seems low, unlike non-glacial environments. This implies that most of the excess solutes mobilized by storms comes from subglacial sources. Increased efficiency of yield of solutes from low water/rock ratio subglacial weathering environments persists after the isotopic signature of the rainfall event has died away.

A simple conceptual model of the sources of water and solutes agrees with conclusions from attempts at hydrograph separation, that mixing of water reservoirs of fixed solute composition cannot be used for quantitative descriptions of the system. Estimated annual solute yields ( $17 \text{ ton per km}^2 \text{ per m precipitation}$ ) are high, but cannot be readily expressed in purely areal terms because of likely significant losses to the underlying karstic system. A tentative conclusion is that the proglacial environment is overall less efficient at producing solutes than the glacial environment, but more information is required on processes in the early melt season to substantiate this statement. Copyright © 1999 John Wiley & Sons, Ltd.

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### INTRODUCTION

Studies of water chemistry in glacial environments have primarily been aimed at two issues: elucidation of glacial hydrology and quantification of weathering processes. For the former case, much progress has been

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made through the application of systematic sampling regimes (e.g. Richards *et al.*, 1996), the analysis of *in situ* subglacial waters (e.g. Tranter *et al.*, 1997), and the experimental dissolution of suspended sediment (e.g. Brown *et al.*, 1996; Collins, 1995a). It now appears that, although it is qualitatively useful to distinguish dilute 'quickflow' and more concentrated 'delayed flow' waters, the composition of neither component is fixed in time or space (Sharp *et al.*, 1995a). The controls on the weathering reactions causing release of solutes from solid materials in glacial environments are now also becoming much better understood. These include the preferential reactivity of phases such as calcite and pyrite, and the importance of the nature of proton supply and its partial control by gaseous diffusion processes (e.g. Raiswell, 1984; Drever and Hurcomb, 1986; Tranter *et al.*, 1993; Fairchild *et al.*, 1994a). Furthermore, in spite of the absence of soils, glacial environments are seen to be important contributors to weathering-related global fluxes of solutes and atmospheric carbon dioxide (Sharp *et al.*, 1995b).

Enhanced delivery of weathering-derived solutes to the oceans during deglaciation has been identified by Kump and Alley (1994) as a likely mechanism to explain the observed increase in preservation of marine pelagic fossils in the 12 to 9 ka interval (Broecker and Peng, 1987). During such times, the proglacial environment may assume particular importance as a solute source, yet there is a dearth of information on the extent to which the geochemistry of waters discharging from glacial outlets is geochemically modified downstream through the proglacial environment, or on the occurrence of distinctive processes in such environments. The question is whether the increased area of proglacial environments tends to increase solute yields during deglaciation or whether, as suggested by Sharp *et al.* (1995b) in relation to CO<sub>2</sub> consumption, it is the discharge pulse caused by excessive melting which is the significant factor, or both. The hydrology of glacierized catchments is as yet too incompletely understood to satisfactorily answer this question. For example, in the intensively studied Haut Glacier d'Arolla, Switzerland, Gurnell (1993) identified the presence of four water storage reservoirs by analysis of flow recession data from a weir 1 km from the glacier's snout, but it was not possible to characterize the proglacial part of the basin because of its limited discharge in the late summer period. Axtmann and Stallard (1995) compared adjacent streams from glacierized and nonglacierized catchment areas and concluded that cationic yields were somewhat higher in the former, but their results are not directly scaled for precipitation per unit area. Here, we contribute to this theme by presenting hydrochemical data in relation to a simple qualitative model representing the carbonate-based Glacier de Tsanfleuron, Switzerland and show how the glacial and proglacial parts of the system behave in delivering solutes during the late melt season. This site is of particular interest because of the diversity of its proglacial environments and the reactivity of its glacial debris (Souchez and Lemmens, 1987; Fairchild *et al.*, 1994a,b).

Figure 1 illustrates the geography of the glacier's environs. Much of the glacier terminates on a karstic limestone plateau (Figure 1) the level of which is close to the boundary between the top of a massive pure Cretaceous (Urgonian) limestone and thin-bedded impure Tertiary limestones. The NE tip of the glacier is a lobe which occupies a valley excavated into a geological syncline of these lithologies, bounded to the north by a thrust boundary with impure Cretaceous (mainly Hauterivian) lithologies which form a cliff on the north glacial margin (see geological map in Fairchild *et al.*, 1994a). The glacier has retreated some 1500 m from its Little Ice Age limit of 1855–1860 and the lobe now terminates in a valley floored by a partly eroded basal till layer up to 2 m thick, partly covered by flutings and recessional moraines. The main meltstream occupies the centre of this valley, flanked by short 'northern' and 'southern' tributaries (Figure 1).

A conceptual model of this site is presented in Figure 2 and is divided into three glacial environments (supraglacial, englacial and subglacial) and the proglacial fluvial environment in the valley to the east. The system is underlain and flanked to the south by limestone karst. Once water enters this karst it is unlikely to re-emerge because of the vertical karstic development of some hundreds of metres. Figure 2a illustrates solute sources qualitatively ranked according to their importance (available mineral surface area) and Figure 2b illustrates how these solutes are dispersed by depicting the water sources, fluxes and reservoirs. By separating the sources of water and solutes, Figure 2 draws attention to those factors which can lead to variable composition of the water leaving the glacier (Tranter *et al.*, 1993; Brown *et al.*, 1994; Sharp *et al.*, 1995a) and joining the main meltwater stream in the proglacial fluvial environment. In this context, quickflow waters are those which pass through englacial and subglacial channels to the main meltstream (possibly with brief

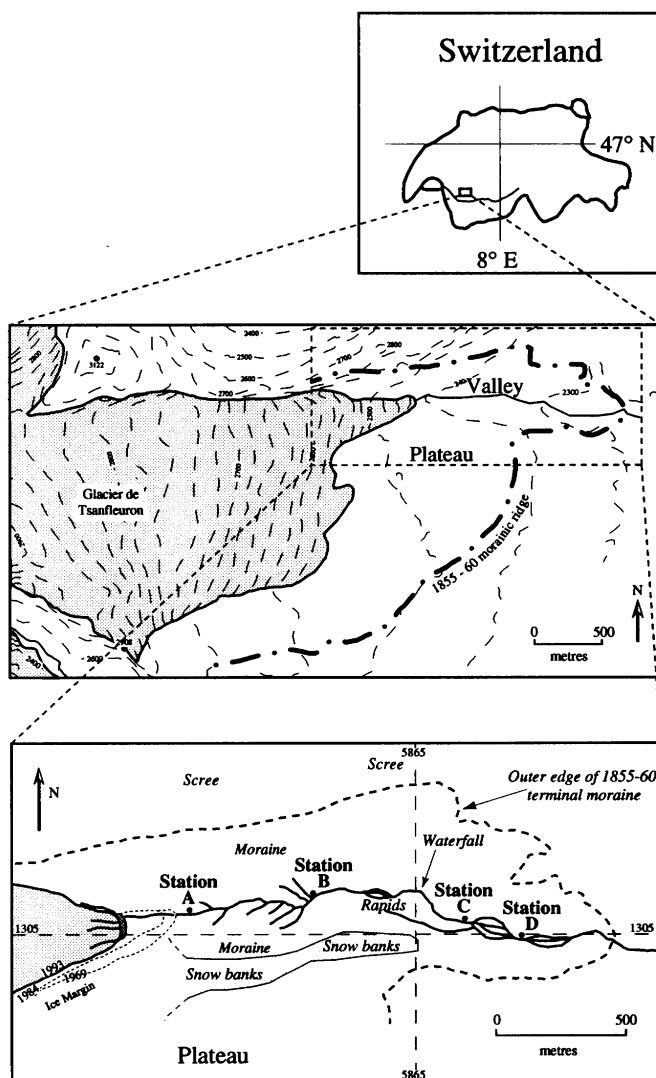


Figure 1. Location map of the environs of the Tsanfleuron glacier including the location of sampling stations A, B, C and D on the main meltstream. 'Northern' and 'southern' tributaries of the text and figures are the short streams shown between stations A and B, and a longer one reaching the main meltstream below station C (this is referred to as 'clear southern tributary' on Figure 4)

storage in a small lake at the glacier snout), or pass directly into the karst aquifer, or run off the valley sides from rain or snowmelt sources. Delayed flow components spend time in a 'distributed system' (Shreve, 1972) at the ice-bed interface, or as porewater in till (e.g. Stone and Clarke, 1996), or in the proglacial fluvial environment as moisture held by capillary forces at the surface. At the ice-bed interface, the reservoir identified as 'film' represents a fluid film on bedrock in the plateau area which in part drains into a linked cavity system (Sharp *et al.*, 1989).

Figure 2 omits certain features related to snowmelt, particularly its storage in the firn reservoir (Fountain, 1996) and preferential routing into a distributed system before the opening of channels later in the melt season (Richards *et al.*, 1996). Nevertheless, it illustrates that the system is complex, and there is necessarily a trade-off between solute and water availability. For example, till porewaters are in contact with large surface areas of mineral matter, but solute acquisition can be limited by exhaustion of aqueous reactants and slow water flow. Solute supply from supraglacial sediment is limited by the rarity of such material, whereas bedrock dissolution is widespread but most of the solutes enter the karst aquifer. Dissolution of suspended sediment is

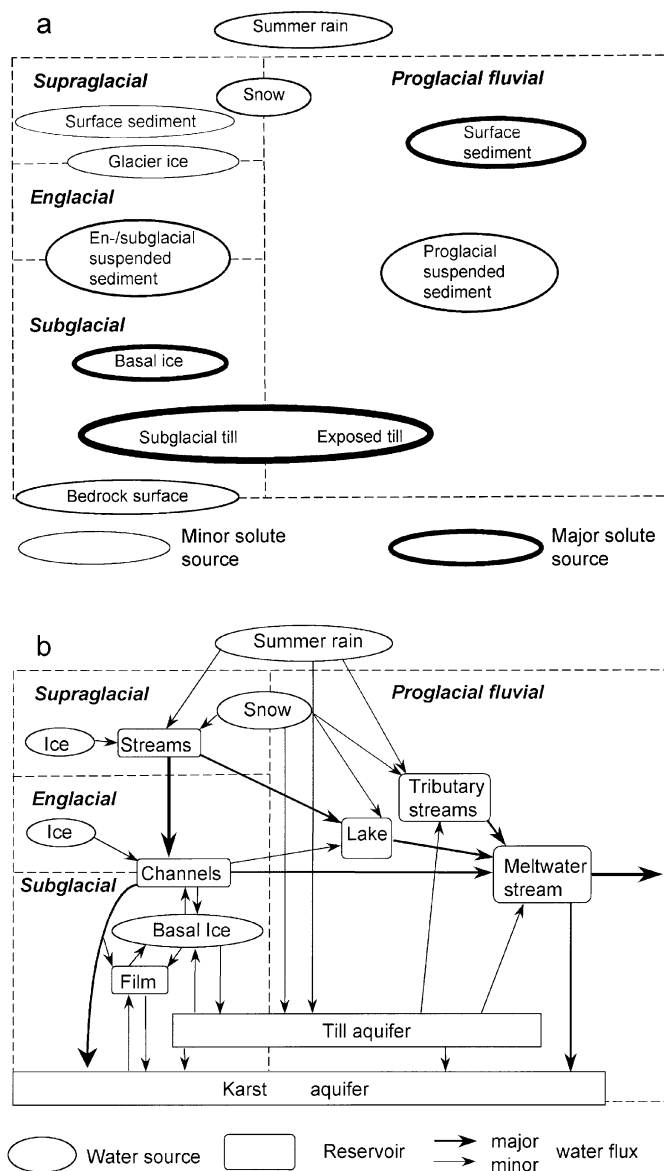


Figure 2. Schematic representation of (a) solute sources and (b) water sources, reservoirs and fluxes at the Tsanfleuron glacier. See text for discussion

limited mostly by suspended sediment concentrations and short reaction times, whereas the transfer of solutes from proglacial surface sediment is intermittent as it relies on flushing by snowmelt or rain.

Hydrological/hydrochemical studies of proglacial environments are not well developed compared with those of other fluvial environments, partly because of their remoteness, but also because of the necessity for systematic measurements of change of stream water chemistry to take account of the diurnal rhythms of snow-and icemelt. These rhythms vary from day to day because of weather conditions and longer-term seasonal changes linked to changing properties of the glacier surface. Hydrochemical data available to date allow us to suggest some ways of characterizing different sources of water and solutes and to illustrate which processes appear to be important and deserving of further study. We will not discuss details of the carbonate

system, since this is considered at length in Fairchild *et al.* (1994a). A companion paper (Fairchild *et al.*, 1999) quantifies the interaction of suspended sediment with meltwater using data from a single 24 h period of systematic collections.

## METHODS

A database of 200, mostly partial, analyses of meltwater, ice and snow, collected in the latter part (July–September) of various melt seasons (Fairchild *et al.*, 1994a) is supplemented by 200 new analyses of samples collected in August 1993 and August 1994, mainly representing systematic collections of the main meltstream chemistry, but including also some tributary stream, snow, basal ice and rain samples. Additionally, in 1994 continuous measurements of electrical conductivity were made at different sites in the main meltstream using a data logger. Procedures follow those of collections in 1990 and 1991, described by Fairchild *et al.* (1994a), except where otherwise stated. Samples were passed by suction through a  $0.45\ \mu\text{m}$  filter and pH and alkalinity measured in the field. Separate aliquots were taken for analysis of cations (acidified aliquot), anions, and hydrogen and oxygen isotopes. Analysis of cations and silica was by ICP atomic emission spectrometry and of anions by ion chromatography. Detection limits and precisions are typically around  $0.1\ \text{mg/l}^{-1}$  for Ca, Mg, Na, K and Si,  $0.02\ \text{mg/l}^{-1}$  for  $\text{SO}_4$ ,  $\text{NO}_3$  and Cl, and  $0.002\ \text{mg/l}^{-1}$  for Sr. Concentrations of ions are presented in units of milliequivalents (meq) per litre (concentration in  $\text{mg/l}^{-1}$  divided by the formula weight multiplied by the ion charge) which represents a measure of the concentration of electrical charge provided by each species. The parameter alkalinity, measured by acid titration, represents the sum of concentrations of the ions  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  and has a precision of  $0.02\ \text{meq/l}^{-1}$ . Charge balance errors (difference between cations and anions, divided by their sum) were normally less than 5 per cent.

Analysis of  $\delta^{18}\text{O}$  was carried out on nearly all 1993 and 1994 samples, and a subset was also analysed for  $\delta\text{D}$ .  $\delta^{18}\text{O}$  was measured from  $\text{CO}_2$  equilibrated with 2 ml of water using a VG Isoprep 18 automated system.  $\delta\text{D}$  was determined on hydrogen gas prepared according to the method of Coleman *et al.* (1982). Results are reported as  $\delta^{18}\text{O}_{\text{V-SMOW}}$  and  $\delta\text{D}_{\text{V-SMOW}}$  with overall analytical reproducibility of  $\pm 0.1$  per mil and  $\pm 2$  per mil respectively.

In 1994, stream discharge was measured during systematic analyses at each station by calibrating measurements of variation in stage (directly measured by a rod) to discharge using calibrations obtained from salt-dilution experiments. Discharge was predicted from stage by means of a power function with  $r^2$  values of 0.92 to 0.96 at different sites. Errors on discharges are around  $\pm 10$  per cent within the calibration range of  $0.02$  to  $0.4\ \text{m}^3/\text{s}^{-1}$ . The gravel stream bed was not mobile in this range of discharges.

Two kinds of weathering experiments were carried out in addition to those reported in Fairchild *et al.* (1994a). Powders of typical rock types were prepared by crushing in a mill to a median size around  $30\ \mu\text{m}$ . Cation yields from such powders to solution were determined on non-agitated slurries (equal weights of powders and deionized water) left for 24 h at room temperature. Following centrifugation and removal of supernatant water, more water was added and the slurry remixed. This was repeated several times, for periods of 24 h or 20 days. The second type of experiment was designed to study sulphate release. Basal ice from the north flank of the glacier was melted in the field and material  $>20\ \mu\text{m}$  was filtered off and weighed. The  $<20\ \mu\text{m}$  material was kept in suspension and returned to the laboratory and refrigerated. In the laboratory two months later, aliquots of the suspension were taken, and the appropriate amount of coarser fraction added to restore the original fluid–sediment characteristics. An initial aliquot was then filtered and analysed for sulphate and cations, and two other aliquots were stored without agitation at  $4^\circ\text{C}$ , and filtered and analysed for sulphate and cations after four days and two months.

## WATER SOURCES

Figure 2 identifies the water sources in the area as rain, and melt of snow, glacier ice and basal ice. Stable isotopic studies have proved useful elsewhere in characterizing variations in, and suggesting sources of waters (e.g. Theakstone and Knudsen, 1996). Because of atmospheric distillation–condensation processes, the isotopic composition of atmospheric precipitation in a given region tends to fall along a ‘meteoric water

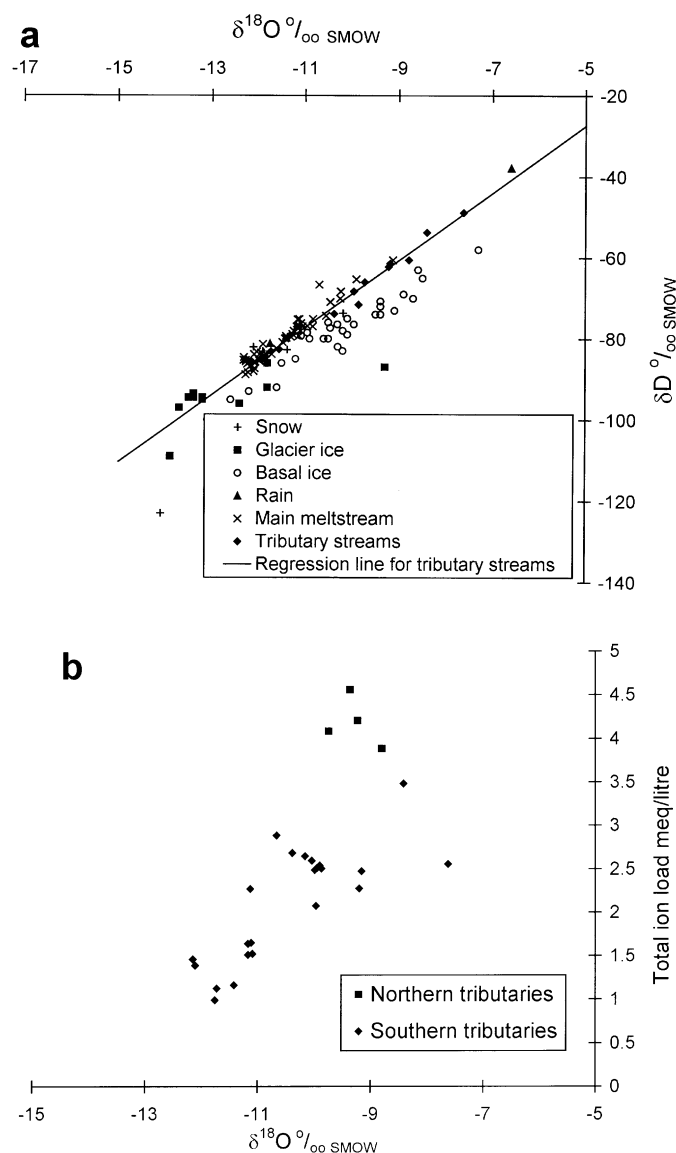


Figure 3. Isotopic data from the Tsanfleuron area. (a)  $\delta\text{D}$ – $\delta^{18}\text{O}$  cross-plot of snow, ice and meltwater including basal and glacier ice data from Hubbard (1992) and glacier ice data from Lemmens *et al.* (1982). (b) Covariation of  $\delta^{18}\text{O}$  with total ion load of tributary waters (including some  $\delta^{18}\text{O}$  data not plotted on (a))

line' on a  $\delta\text{D}$ – $\delta^{18}\text{O}$  cross-plot (Dansgaard, 1964; Gat, 1996), with components forming by higher temperature condensation, such as summer rains, having isotopically heavier values than, for example, winter snows. Snow tends to become lighter with altitude by around 0.6–1 per mil per 100 m (Niewodniczanski *et al.*, 1981). The composition of glacier ice is expected to reflect that of the bulk snow surviving summer melting, i.e. above the ablation zone of the glacier, whereas snowmelt can be significantly lighter than the bulk snow (Arnasson, 1969; Souchez and Lorrain, 1991). In contrast, basal ice samples typically deviate systematically from the composition of glacier ice, along a straight line of lower slope than the meteoric water line, because of refreezing processes (Jouzel and Souchez, 1982; Souchez and Lorrain, 1991; Hubbard and Sharp, 1995).

Figure 3 presents results of stable isotopic analyses, excluding some water samples from pools exhibiting signs of evaporation (Fairchild *et al.*, 1994b). A meteoric water line was estimated by regression of data collected in the period 23–27 August 1994 from tributary streams (Figure 3a), whose water is derived from a mixture of snowmelt and snow- and rain-derived seepage water. The resulting equation is:  $\delta D = 8.3 \delta^{18}O + 14$  ( $r^2 = 0.98$ ) (with standard errors on slope of  $\pm 0.2$  and on intercept of  $\pm 2$ ) which compares with a slope of 8.17 and an intercept of +10.35 per mil in the latest global fit to the meteoric water line (Rozanski *et al.*, 1993). The oxygen isotope composition of these tributary waters varies sympathetically with total ion content (Figure 3b). Since the collections were made during fine weather, the dilute samples should reflect a dominance of snowmelt: these streams average around  $-12$  per mil. In contrast, the concentrated flows which have low discharge and are spring-fed, have compositions around  $-8$  to  $-9$  per mil (significant evaporation is precluded by their proximity to the meteoric water line). Since these values are much heavier than recorded snow, but lighter than one of the summer rainfall samples, the isotopic values of spring-fed streams are taken as implying rain recharge of the sediment aquifer.

Co-isotopic data from the main meltstream are sampling mostly snow- and icemelt from higher elevations, and lie close to the meteoric water line defined by the tributaries (Figure 3a). The heavy samples were all collected during or following rainfall events, which is consistent with rainfall input being largely responsible for the covariation, but it is also implied that the lighter, higher elevation meltwater sources lie on the same meteoric water line. Indeed, a cluster of glacier ice analyses at around  $-13$  to  $-14$  per mil  $\delta^{18}O$  (Lemmens *et al.*, 1982) plots co-linearly with the meltstream samples and may therefore be representative of the bulk glacier, in contrast to other individual samples of snow and glacier ice lying below this line on Figure 3a. The fact that meltstream samples never drop below around  $-12.2$  per mil during the study periods probably reflects inputs of lower altitude snowmelt and rain. Diurnal variations in hydrogen and oxygen isotopes recorded elsewhere (e.g. Behrens *et al.*, 1979; Theakstone and Knudsen, 1996) are not evident at Tsanfleuron in the late melt season. Since the top of the glacier is only 400 m above the proglacial environment, this limits the original altitude-related isotopic variation. As expected, basal ice samples show systematic deviations from the meteoric water line (Figure 3a). Basal ice would not be expected to provide a major source of meltwater, although solute supply from this source may be significant because of its high debris content (Hubbard *et al.*, 1996) as indicated on Figure 2.

Ionic composition is another potential means of distinguishing water sources, in particular by use of nitrate and chloride which are not expected to be derived from rock weathering (Sharp *et al.*, 1995b). Partial melting of snowpacks is known to produce acid waters with early melt season yields of nitrate being particularly high (e.g. Jenkins *et al.*, 1993). However, by the late melt season, these effects will not be prominent unless water stored early in the season is still being released under low flow conditions. The only systematic effects noted in our meltstream data are increases in nitrate during low flows, in contrast to low nitrate abundance in ice.

## SOLUTE SOURCES

### *Atmospheric precipitation*

Atmospheric precipitation is a solute source (Figure 2). Chloride is generally assumed to be marine-derived, which implies that other ions present in precipitation should have a marine-derived component proportional to their abundance relative to chloride in sea water (assuming no HCl pollution). This marine aerosol component has been calculated for the various ions in the Tsanfleuron samples on this basis, but it is significant only for sodium, where it represents the main ion source. Weathering-derived sodium, by contrast, can only be distinguished in samples with the highest ionic loads (Fairchild *et al.*, 1994a). Both pollution and weathering of atmospheric dust are also important contributors of ions (sulphate, nitrate and cations) and silica to atmospheric precipitation, but these components can be highly variable from one event to another. There are insufficient data currently available to provide reliable mean values for these species in precipitation. Table I illustrates the decrease in significance of the predominantly atmospherically derived species nitrate and chloride as total ion load increases.

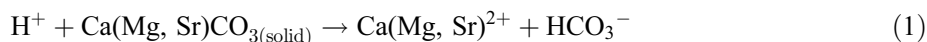
Table I. Summary of anionic compositions of Tsanfleuron (melt)waters.

Total ion load (meq l <sup>-1</sup> )	Median (%) of anion load contributed by		
	(NO <sub>3</sub> <sup>-</sup> + Cl <sup>-</sup> )	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
<1	3	93	4
1–2	2	87	11
>2	1	75	24

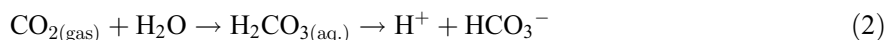
### Carbonate and sulphide weathering

Weathering of limestones provides the bulk of solutes in the system. Figure 4 illustrates a covariation of sulphate, magnesium and strontium with calcium in meltwaters and Table I summarizes how the anionic composition progressively shifts as ionic loads increase. Essentially the anions are labelling the sources of protons in the waters.

The most dilute waters (<1 meq l<sup>-1</sup> total ion load) are overwhelmingly dominated by alkalinity created by CaCO<sub>3</sub> dissolution:

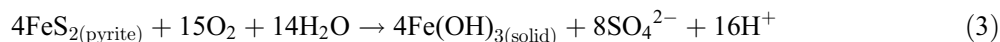


Calcium loads of up to 0.4–0.5 meq l<sup>-1</sup> can be created within minutes in the laboratory by shaking calcite powders in water in partly air-filled bottles. The proton (H<sup>+</sup>) source in this case is aqueous CO<sub>2</sub>:



The aqueous CO<sub>2</sub> is rapidly exhausted and is only slowly resupplied, hence its availability limits dissolution rates (Raiswell, 1984; Tranter *et al.*, 1993). Such dilute meltwaters have relatively low ratios of Mg/Ca and Sr/Ca which are close to the composition of the CaCO<sub>3</sub> which is being dissolved. This is characteristic of weathering in high water/rock (W/R) ratio environments (Fairchild *et al.*, 1994a).

Moderate total ion loads (1–2 meq l<sup>-1</sup>), which characterize the bulk of the meltstream waters, tend to have significantly higher fractional sulphate concentrations (Table I). The sulphate arises from pyrite oxidation:



The acidity created provides a proton source for further calcite dissolution without the requirement for more CO<sub>2</sub> input from the atmosphere. Where ionic loads are high (>2 meq l<sup>-1</sup>), sulphate becomes highly significant (Table I). Such waters have lower pH and have a higher partial pressure of CO<sub>2</sub> than the atmosphere (Fairchild *et al.*, 1994a).

Results of experimental weathering of melted basal ice samples are summarized in Table II. Significant increases in sulphate are found during progressive weathering and are highest where there is a large

Table II. Results of weathering experiments of melted ices. Sediment size distribution refers to % coarse (&gt;63 µm) – % medium to coarse silt (20–63 µm) – % fines (&lt;20 µm)

Sample	Sediment mass (g) per litre water	Sediment size distribution	Sulphate yield (meq l <sup>-1</sup> )		Sulphate yield (62 days) per 100 g sediment	Sulphate/Ca equivalent ratio			Mg/Ca equivalent ratio		
			4 days	62 days		Initial	4 days	62 days	Initial	4 days	62 days
1	28	68–22–10	0.03	0.08	0.28	0.06	0.07	0.08	0.07	0.06	0.06
2	48	90–7–3	0.03	0.1	0.20	0.05	0.06	0.09	0.05	0.06	0.09
3	52	9–22–69	0.19	0.38	0.73	0.32	0.39	0.46	0.23	0.24	0.30
4	66	88–7–5	0.04	0.19	0.29	0.01	0.03	0.12	0.02	0.04	0.08
5	800	93–4–3	0.42	0.95	0.12	0.03	0.27	0.45	0.05	0.27	0.31
6	1070	91–5–4	0.35	1.20	0.09	0.15	0.29	0.63	0.17	0.22	0.31



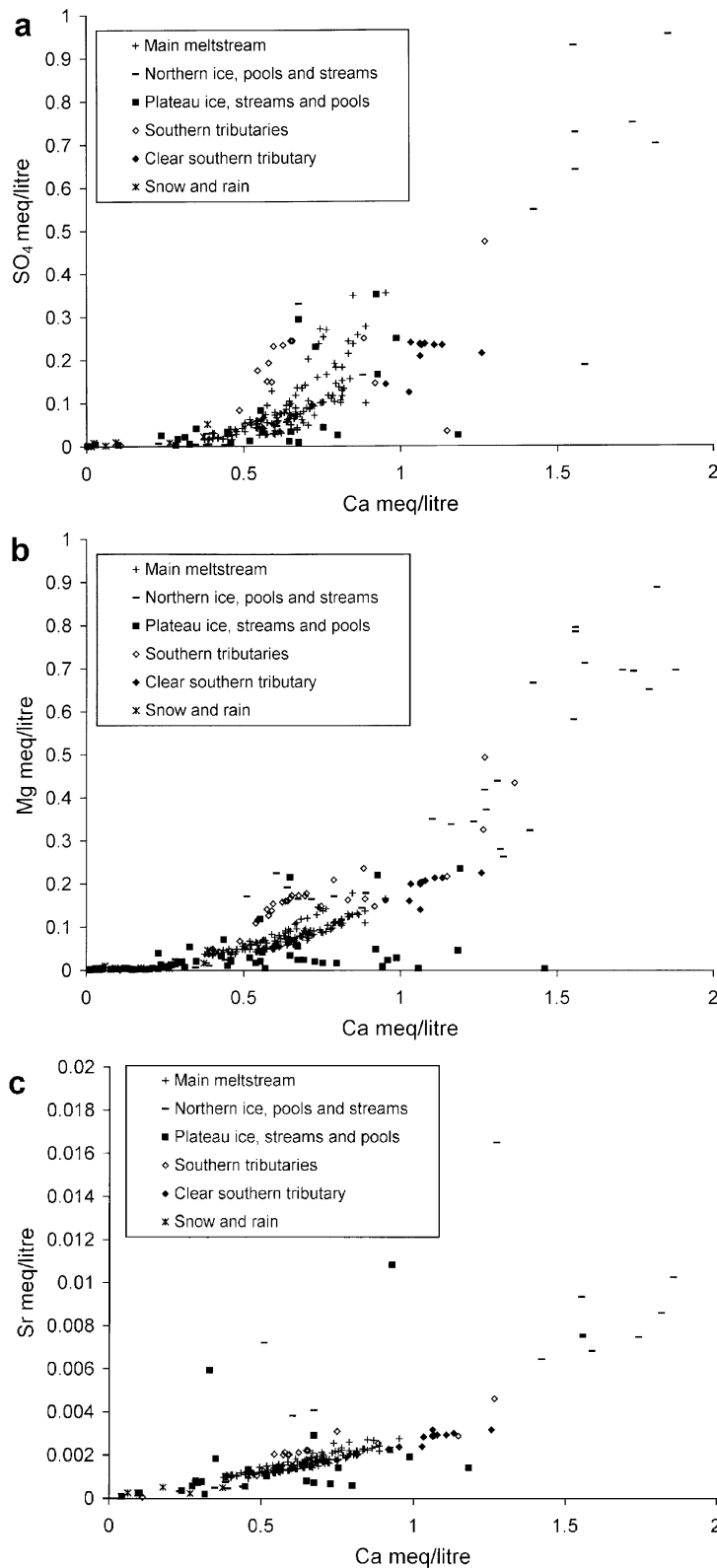


Figure 4. Cross-plots against Ca of solutes derived principally by weathering; (a) sulphate; (b) magnesium; and (c) strontium

proportion of fines. Sulphate yields should be proportional to exposed pyrite surface area (Nicholson *et al.*, 1988) which will vary significantly from place to place. Sharp *et al.* (1999) carried out bacteriological studies on Tsanfleuron materials and deduced that pyrite oxidation may be bacterially mediated, since bacterial counts increase greatly during the incubation and the inferred rates of pyrite oxidation are one to two orders of magnitude higher than anticipated from inorganic weathering (Nicholson *et al.*, 1988). The highest values of  $\text{SO}_4/\text{Ca}$  encountered in field measurements (0.33–0.5, Figure 4a) would seem to require at least some months of sediment contact. Also, given that meltwaters are likely to be diluted by rain, snow or icemelt, it seems that periods of time of the order of weeks to months are required to reach the high sulphate concentrations found in many stream samples (Figure 4a).

At high solute loads the Sr/Ca and especially Mg/Ca ratios are found to be high (Figure 4b, c), significantly higher than in the acid-soluble fraction of bulk limestones (Fairchild *et al.*, 1994a). This was originally attributed to low W/R weathering under which incongruent dissolution of relics of metastable carbonate phases (aragonite and Mg-calcite) occurs (Fairchild *et al.*, 1994a). Probable aragonite relics (electron microprobe analytical spots of up to 6000 ppm Sr) have subsequently been detected in originally aragonitic fossils in a Tsanfleuron Tertiary limestone sample, but Mg-calcite was not found by microprobe analysis of originally Mg-calcite echinoderm fragments in a Hauterivian limestone. Fairchild and Killawee (1995) presented results of experimentally leaching carbonate powders and showed that even pure calcite can show significant non-congruent dissolution effects, yielding preferential release of Mg and Sr relative to Ca by factors of 3 to 10. The enrichment in Mg and Sr in Tsanfleuron waters is therefore attributed mainly to non-congruent dissolution of calcite in low W/R ratio weathering environments. Such dissolution behaviour should be a feature of any glacial limestone terrain, but at Tsanfleuron there are also local concentrations of aragonite which yield outliers in meltwater data with high Sr content (Figure 4c).

The results in Table II illustrate that Mg/Ca ratios also rise given longer contact times, but the rate of rise is generally less than the  $\text{SO}_4/\text{Ca}$  ratio. Similar results were found for Sr/Ca. Other new experiments, but on slurries of powdered rock samples (see methods), showed that in the case of a 20 day leach, Mg/Ca and Sr/Ca ratios were some 25 per cent higher than in preceding and following 24 h leaches. High Mg/Ca and Sr/Ca have previously been found to be a feature of short-term leaching experiments on powdered rock samples (Fairchild *et al.*, 1994a; Fairchild and Killawee, 1995), but only under low W/R ratio conditions. In principle, any waters with high Mg/Ca or Sr/Ca and low sulphate should reflect short contact time under low W/R conditions. Comparison of Figure 4a and b illustrates that there are no such waters. The implication is that the hydrological conditions which lead to low W/R ratio weathering permit only slow transmission of fluid. Hence any one of sulphate, Mg or Sr (or Mg/Ca or Sr/Ca) can be used as proxies both for the occurrence of low W/R ratio environments and for weathering time. Given that sulphate continues to rise by pyrite oxidation at a faster rate than either Mg/Ca or Sr/Ca, waters that have undergone unusually long contact times may be distinguishable as having high Mg but relatively low Mg/ $\text{SO}_4$  ratios.

In addition to this conclusion there are also some differences caused by spatial variation of materials undergoing weathering. A number of low-Mg samples from the plateau area (Figure 4b) can be attributed to contact only with Urgonian limestone which contains up to an order of magnitude less Mg than the other limestones (Fairchild *et al.*, 1994a). The spring-fed clear-water southern tributary (Figure 4) is depleted in Mg and sulphate compared with the bulk meltstream which again probably arises from relatively more contact with the pure Urgonian limestone which forms the plateau karst. Conversely, other southern tributaries are enriched in sulphate, Mg and Sr compared with bulk meltwaters and probably contacted more of the dark-coloured pyritic Tertiary limestones. Northern ice (as used in the experiments of Table II), pools and streams will have contacted mainly or entirely Hauterivian debris which is rich in pyrite, as well as Mg and Sr. It is evident that the subglacial weathering of such materials is required to explain the upper end of the range of compositions of waters from the main meltstream (Figure 4).

Silicate weathering has been neglected in the previous discussion, but the impure limestones of the Tertiary and Hauterivian also carry significant silicates, chiefly quartz, but with up to 70 percent illite and chlorite in the  $<2\ \mu\text{m}$  fraction. In the most concentrated northern meltwaters, ratios (of equivalent ions and mg/litre Si) for Ca:Mg:Na:K:Si are typically 2:1:0.01:0.02:0.03:1, the Na value having been corrected for marine aerosol. These ratios are typical of those obtained from 24 h leachates of slurried crushed Hauterivian and

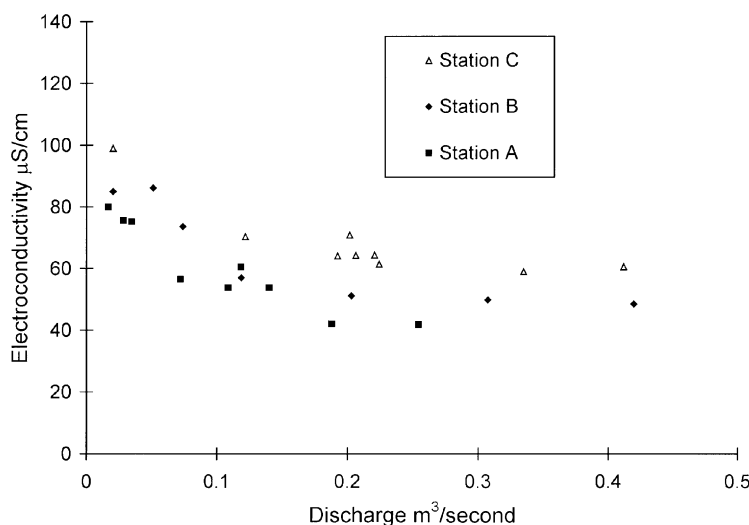


Figure 5. Variation of electroconductivity (uncorrected for temperature) with discharge in the main meltstream (data collected in period 23–28 August 1994). Discharges were measured by salt dilution experiments. Calcium concentration ( $\text{meq l}^{-1}$ ) are approximately 1/177 that of electroconductivity. These data cannot be modelled by mixing of two constant reservoirs

Tertiary bedrocks except that the ratio of Si to other species is typically five times higher in the slurries. The experimental slurries also have six times higher absolute concentrations. Over such short time periods, silicate lattice dissolution is likely to be much less important than exchange reactions. Silica may be released by quartz, illite or chlorite dissolution, whereas potassium (Lemmens and Roger, 1978) and some magnesium derive from clays; and sodium comes both from carbonates (Fairchild *et al.*, 1994a) and silicates, but it is not possible to quantify the relative amounts at present. In most meltwaters, the concentrations of K, Si and Na are much lower, and smooth patterns of variation with time are not found in systematic sampling of the main meltstream, suggesting a combination of inherent variability, and problems of analytical resolution since concentrations are commonly close to the detection limits.

## HYDROCHEMICAL VARIATIONS IN THE MAIN PROGLACIAL MELTSTREAM

### *Summary variations in electroconductivity*

Figure 5 summarizes the results of discharge determinations made by salt dilution techniques compared with the baseline electroconductivity reading around the time of discharge measurement. The variations in discharge span more than an order of magnitude and show decreases in conductivity with increasing discharge at a given site. This reflects a higher proportion of dilute quickflow waters during daytime peak flows, or a shorter mean residence time of meltwater. Downflow sites have higher solute concentrations, reflecting input of more solute-rich waters in the proglacial environment and in-stream weathering of suspended sediment. The relative magnitude of the proglacial water fluxes, during fine weather at least, is less than the  $\pm 10$  per cent error of determination of discharge by the salt dilution method as no consistent increases in discharge were found downflow.

### *Time series data: introduction*

Study of time series data allows the impact of discrete events, such as heavy rain, to be quantified in relation to the normal patterns of diurnal variation. Additionally, study of main meltstream chemistry at two sites over the same time period allows the addition of solutes in the proglacial zone to be assessed. Systematic observations of the variation in discharge, calcium,  $\delta^{18}\text{O}$ , sulphate and nitrate in the main meltstream over

four sampling periods are presented in Figure 6. Magnesium and strontium variations (not shown) are similar to sulphate. Sampling period 1 was for 24 h at a single station (D, Figure 1) in August 1993, for which no discharge information is available. It followed four days of dry conditions, but was influenced by nocturnal rain. Sampling periods 2 to 4 were in August 1994. Period 2 was a 24 h period (21–22), at two stations, one (A) 200 m from the meltstream source and the other (C) 1200 m downstream. Little rain had been experienced during the previous four days, but a violent nocturnal thunderstorm occurred during the study. Period 3 was during the morning of 25 August at station A and was less directly affected by rain, although there had been some the previous day. Finally, period 4, a 24 h study (26–27) followed some rain the previous day, but was itself unaffected by rain.

#### *Sampling periods 3 and 4: normal conditions*

Sampling period 3 (at station A) illustrates a rise in discharge and fall in ion concentrations (after 10:00) that occur as ice- and snowmelt increase during the morning (Figure 6). The  $\delta^{18}\text{O}$  values are higher than during the following day at stations B and C in sampling period 4 (Figure 6b). This represents the recession of runoff input derived from rain on previous days which is further illustrated by the fall in isotopic values at the beginning of sampling period 4 (Figure 6c) which is independent of discharge variations (Figure 6a).

Sampling period 4 illustrates a full 24 h cycle. Smooth variations in solute concentrations are displayed, peaking at lowest flows, reflecting a longer mean residence time of waters under these flow conditions. This pattern is typical of fine weather conditions because it matches the pattern of variation of electrical conductivity on a number of other days when systematic water sampling was not performed. There is a significant rise in calcium in the tributary-free reach of the river between stations B and C, which can be attributed largely to dissolution of suspended sediment. Quantification of sediment and fluid characteristics indicates that the small (5–10 per cent) rise in sulphate could be accounted for if 0.7–1.8 per cent of the water at C were derived by seepage of solute-rich water similar to that found at till springs (Fairchild *et al.*, 1999). The Ca flux from calcite dissolution varied little with discharge despite an order of magnitude fall in suspended sediment concentration between high and low flows: this reflects a ceiling on calcite dissolution rates forced by  $\text{CO}_2$  transport and hydration kinetics at high flows (Fairchild *et al.*, 1999).

The first 12 h of sampling periods 1 and 2 also represent 'normal' conditions and show similar patterns of variation. In the proglacial zone, solutes are also added by tributaries between A and B, and between C and D, as well as by bank seepage as discussed above. The addition of solutes between 2A and 2C is discussed in the section on solute yields.

The rise in nitrate concentrations during nocturnal low flows indicates that the delayed flow components of the subglacial environment have higher nitrate concentrations than the snow- and icemelt-dominated daytime flows. The implication is that snowmelt-derived nitrate is stored in the subglacial distributed flow system, as is observed in the Haut Glacier d'Arolla (Tranter *et al.*, 1997).

#### *Sampling periods 1 and 2: rain-influenced conditions*

Sampling period 1 displays a rain-induced shift in oxygen isotopic composition of the river water (Figure 6c) of 2.8 per mil at 23:00 h. The  $\delta^{18}\text{O}$  value decays rapidly over a period of 8 h, but there is little corresponding change in chemical parameters (Figure 6b, d) apart from nitrate which increases (Figure 6e). The lack of depression of solute concentrations by rainwater dilution is remarkable and implies that the waters must have picked up significant ion loads en route. We have no discharge data to enable further quantification of these processes.

Sampling period 2 illustrates the typical smooth pattern of variation until after midnight when heavy rain led to a surge in discharge at 01:00 (Figure 6a), together with notable increases in solute loads, although the calcium increase is modest. Although the discharge had fallen greatly by 03:00 h, the isotopes and ion concentrations all peaked at this time. In both sampling periods 1 and 2, nitrate levels were raised significantly in the main meltstream during the period following rainfall (Figure 6e), to much higher levels than found during sampling period 4. A quantitative analysis of these data is given in the next section.

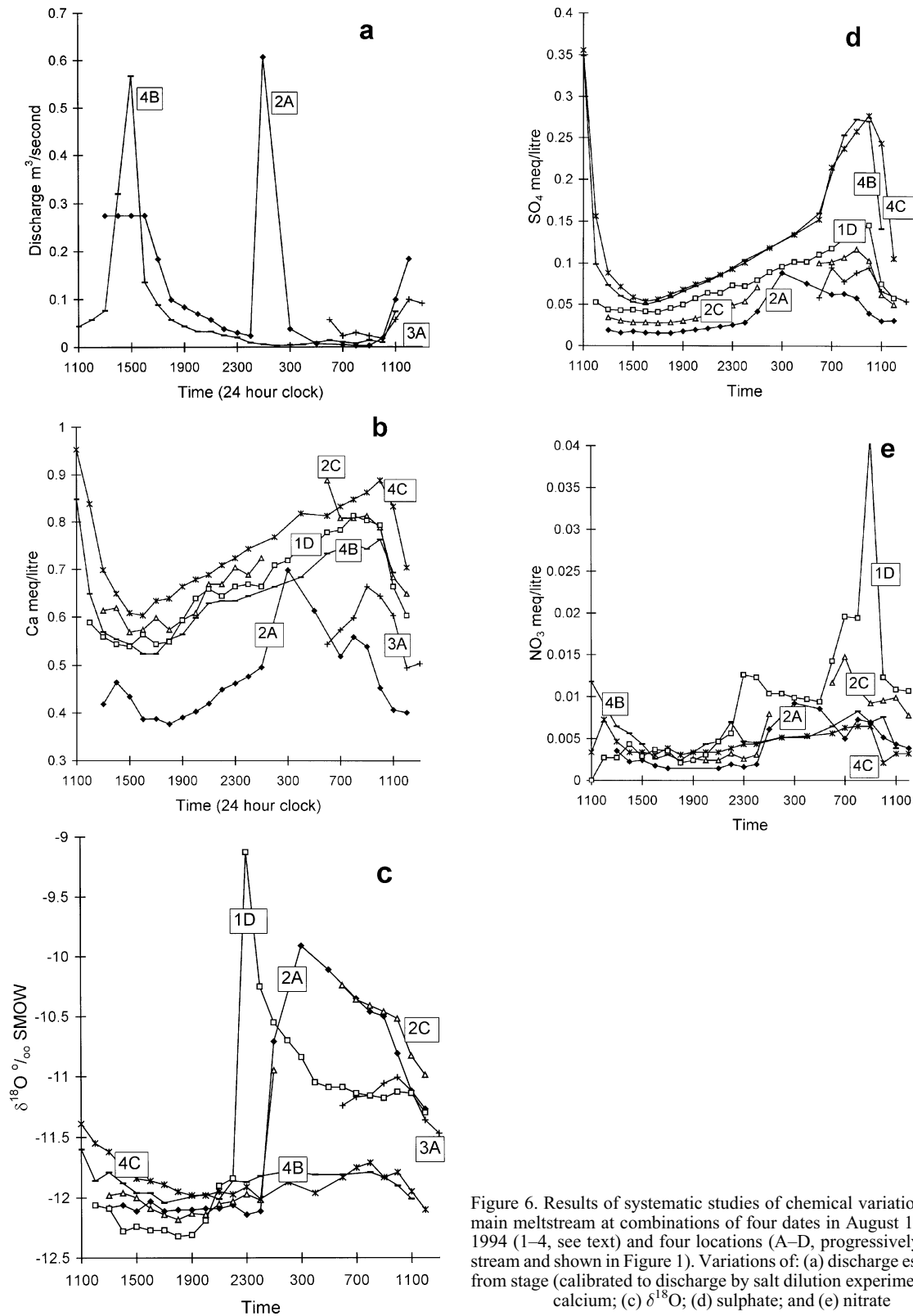


Figure 6. Results of systematic studies of chemical variation of the main meltstream at combinations of four dates in August 1993 and 1994 (1–4, see text) and four locations (A–D, progressively downstream and shown in Figure 1). Variations of: (a) discharge estimated from stage (calibrated to discharge by salt dilution experiments); (b) calcium; (c)  $\delta^{18}\text{O}$ ; (d) sulphate; and (e) nitrate

## HYDROGRAPH SEPARATIONS

*Diurnal flows*

Early hydrologic models (e.g. Collins, 1979) assumed that the mixture of two reservoirs (e.g. quickflow and delayed flow) of consistent composition could explain the diurnal patterns of variation of glacial meltwaters. If such a model has any application to the meltstream it can only be at upstream site A. Figure 7 illustrates cross-plots of Sr with Mg and sulphate from site A. The Sr–Mg data (Figure 7a) are broadly consistent with variable dilution of a concentrated reservoir with a water containing small amounts of Sr and Mg such as could be generated by rapid dissolution of rock debris like that of bulk suspended sediment. However, the sulphate data (Figure 7b) more obviously violate such a simple relationship, even over relatively short periods of a few days. The electroconductivity (EC) data (Figure 5) can also be shown to be quite inconsistent with such an assumption. For a two-component conservative mixing model, expressing total EC flux as the sum of fluxes from the two components:

$$EC_b Q_b = EC_1 Q_1 + EC_2 Q_2 \quad (4)$$

where  $EC$  is solution electroconductivity,  $Q$  is discharge, and the subscripts  $b$ , 1 and 2 refer respectively to bulk mixed solution, the concentrated component and the dilute component, of the mixed solution. The expected value of  $EC_b$  is given by:

$$EC_b = EC_1 Q_1 / Q_b + EC_2 Q_2 / Q_b \quad (5)$$

A plot of  $EC_b$  versus  $Q_b$ , Equation 5 requires mixing lines to be curved, concave to the upper right in Figure 5. By experiment it has been found that no such line will fit data across more than half of the range of observed discharges. To fit all data, the more concentrated component would be required to diminish in concentration, or absolute discharge, or both, at lower bulk discharges, implying less efficient entrainment of solutes from low water/rock ratio weathering environments at low flows. A similar sense of difference at higher and lower discharges was obtained using time series data for the conservative species sulphate (using stage as a proxy for discharge), over a more limited range of discharges. This is consistent with data from other alpine glaciers (e.g. Collins, 1995a; Richards *et al.*, 1996), although Collins (1995b) curiously found the opposite to be the case in the Swiss Gornera meltstream.

Overall, the results are consistent with the nature of the system illustrated in Figure 2 and with theoretical, observational and experimental data obtained elsewhere. A fixed composition of delayed flow waters is not expected because several different reservoirs may exist (as determined by Krawczyk (1992) and Tranter *et al.* (1997) and because continuous evolution of fluid composition should be occurring (Sharp *et al.*, 1995a). In the absence of pyrite, calcite dissolution may be rapid, and limited by saturation, but continued generation of acidity by pyrite oxidation drives increases in the main cations as well as sulphate. A second factor is that since there is no reason to suppose all mixing takes place immediately prior to emergence of the meltwaters, there is likely to be dissolution of suspended sediment after mixing, rendering Ca non-conservative (Sharp *et al.*, 1995a; Richards *et al.*, 1996). This is particularly likely at high flows.

*Storm flows*

Despite a large literature on hydrograph separation during storm flows in non-glacial environments (Buttle, 1994; Kendall *et al.*, 1995b), little information is available on the effects of summer rainfall events in glacial terrains. In mountainous terrains, Klemes (1990) has identified the problems of accessibility, accuracy and representativeness as barriers to hydrological modelling. Although we have only limited discharge information which limits the accuracy of our statements, the use of data from the main meltstream reduces problems of representativeness because it reflects the output from the system as a whole, although at the expense of detailed information on mechanisms. Most hydrograph separation studies have posited two components separated by means of isotopic or chemical analyses, or both. This is acceptable where a

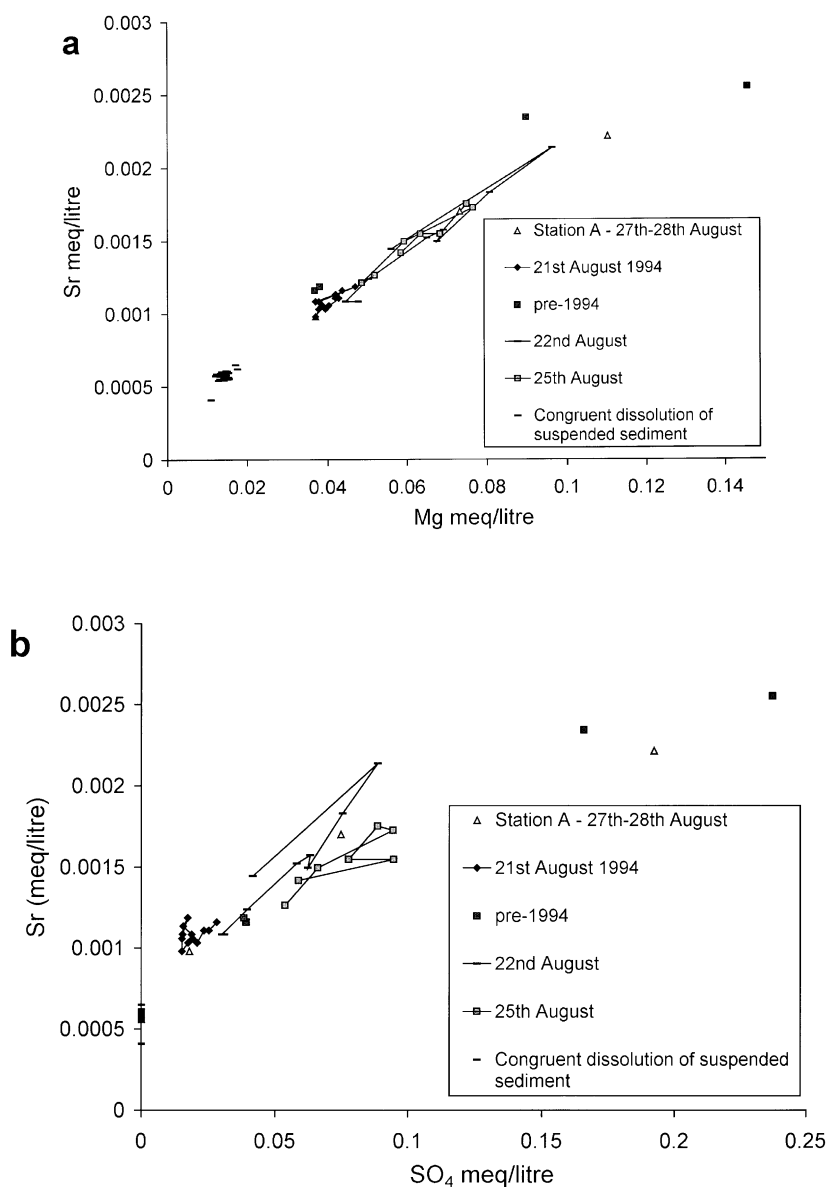


Figure 7. Cross-plots of data from station A in the main meltstream: (a) Sr versus Mg and (b) Sr versus sulphate. Suspended sediment data are inferred compositions of water following congruent dissolution of sediment up to a calcium composition of  $0.4 \text{ meq l}^{-1}$  (calculated from Mg/Ca and Sr/Ca in dilute acid leachates from suspended sediments in main meltstream)

baseflow of uniform composition (Sklash *et al.*, 1976) is clearly distinct from input of rainfall which does not generate solute ions. A number of studies have illustrated that a third (soil) component is required which can be most effectively separated by cross-plots of ions versus  $\delta^{18}\text{O}$  (e.g. Hinton *et al.*, 1994; Kendall *et al.*, 1995b). In the glacial environment, complexity is afforded by the diurnal pattern of variation which provides a sloping baseline to most parameters, and illustrates that the water is clearly drawn from more than one reservoir. Nevertheless, by comparing the composition of this baseflow with that of the new rainwater, the necessity for other factors can be judged.

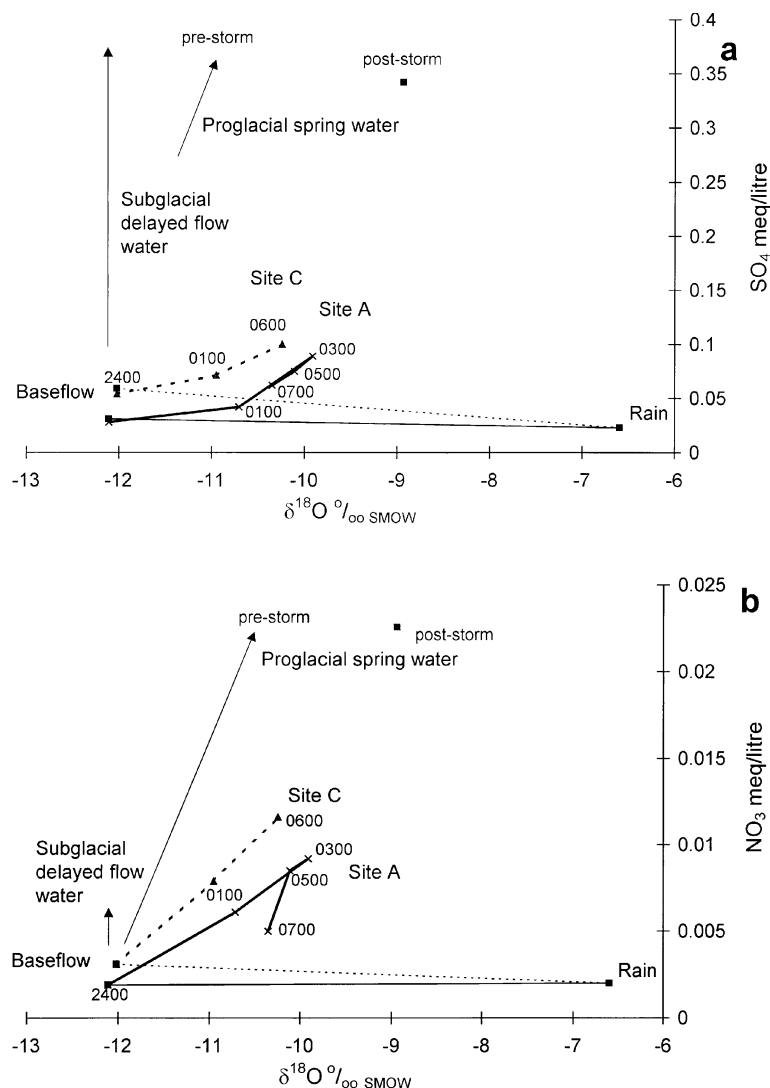


Figure 8. Plots of  $\delta^{18}\text{O}$  versus (a) sulphate and (b) nitrate during sampling period 2, illustrating the varying meltstream compositions immediately prior to and following the rainstorm. Various possible end-members for mixing are shown on the diagrams. Baseflow is the composition of bulk glacial meltwater (extrapolated to 01.00), shown separately for stations A and C. Mixing lines are shown between these baseflow values and the rainwater sample analysed. The vertical arrow denoting subglacial delayed flow indicates that its isotopic composition should be the same as baseflow, whereas its sulphate composition is higher than baseflow, but undefined (possibly as high as  $0.35 \text{ meq l}^{-1}$ ). The arrow labelled 'proglacial spring water, pre-storm', is obtained by extending the join between baseflow at station A and at station C, i.e. assuming that the difference between the two (at night when snowmelt is minimal) was due to mixing with spring water. The sulphate composition of this pre-storm water is also not known with any confidence. The post-storm point is a mean of spring analyses as explained in the text, but has an uncertainty of at least 50 per cent in sulphate concentration. Mixtures of rainfall with the existing baseflow are clearly inadequate to explain the observed chemistries. Sr, Mg and Ca show similar deviations as sulphate from baseflow–rainwater mixing lines. Nitrate, in contrast, shows higher deviations

Figure 8 illustrates cross-plots of sulphate and nitrate with  $\delta^{18}\text{O}$  over a time period covering the rainstorm event during sampling period 2. The enhanced solute concentrations following the storm are notable features and illustrate that mixing of a two-component system is inappropriate even for sulphate which is more geochemically conservative than other components. Increases in solute concentrations as a result of storms are not found in temperate environments, despite the rapid mobilization of ions in soil zones by various processes (Fritz *et al.*, 1975; Mulholland *et al.*, 1990; Hinton *et al.*, 1994). However, the absolute ion concentrations are significantly higher in temperate carbonate terrains. In a badlands catchment, total ion



concentrations of bulk storm flows of at least  $200 \text{ mg l}^{-1}$  (over  $3 \text{ meq l}^{-1}$  calcium) were recorded by Llorens *et al.* (1997), compared with background values of  $250\text{--}300 \text{ mg l}^{-1}$ . The increases in solute concentrations during Tsanfleuron storms can thus be understood as partly reflecting the low precursor solute concentrations.

The excess solutes clearly need to be derived from a low WR ratio weathering source. In the proglacial environment, one can envisage such sources as being groundwater and 'soil' water. Subsurface sources of 'old' water have been shown to make up the bulk of the storm hydrograph in natural non-glacial environments, although the mechanisms of translation of this water to the stream are more difficult to establish (Kennedy *et al.*, 1986; Pearce *et al.*, 1986; Buttle, 1994). In the Tsanfleuron proglacial environment, the sediment consists of massive lodgement till overlain by recessional moraines with a high content of fines and incipient soil development related to a sparse covering of higher plants. Occasional surface salt or carbonate crusts are noted, particularly on clasts. Permeabilities in the range  $10^{-8}$  to  $10^{-6} \text{ m s}^{-1}$  in undisturbed till can be inferred (Parriaux and Nicoud 1990) which is incompatible with rapid subsurface flow. This contrasts with forested till environments where soils and weathered tills are more permeable and may display macroporosity. The composition of groundwater seeps has been estimated by averaging the mean composition of five streams with  $>2 \text{ meq l}^{-1}$  total ions. These data were collected in the period 25–28 August 1994 and are labelled 'post-storm' on Figure 8. However, the seepage water might have been isotopically lighter before the storm. An estimate of possible values of  $\delta^{18}\text{O}$  of seepage before the storm is given by extrapolation of the join of waters at 24.00 h from sites A and D ('pre-storm' on Figure 8). The true  $\delta^{18}\text{O}$  values would be at least as high as indicated because there may have been a contribution from some (isotopically light) snowmelt to the proglacial zone at this time. Near-surface water in incipient soils could have a higher  $\delta^{18}\text{O}$  composition as a result of evaporation, but no appropriate compositions of such water are available (plateau pools in August 1990 varied in  $\delta^{18}\text{O}$  signature from  $-9$  to  $-1$  per mil; Fairchild *et al.*, 1994b). If pre-existing proglacial waters, with compositions similar to streams analysed, were the only source of excess solutes, a total contribution of  $<25$  per cent of the total water volume can be calculated from Figure 8a (and similar plots for Sr and Mg), much less than in non-glacial environments (Fritz *et al.*, 1975; Buttle, 1994; Kendall *et al.*, 1995b). However, if solute-rich porewaters existed near the land surface, or were created by dissolution of surface crusts, the contribution of the land surface to total solutes would be much greater than its contribution to the total volume of water.

Given the difficulties in deriving significant solutes from the proglacial zone, it seems likely that there was a major contribution of solutes from subglacial sources. Under normal conditions this would represent a 'delayed flow' hydrological component. Since there is no regular diurnal variation in  $\delta^{18}\text{O}$  of meltwater, a composition of delayed flow waters around  $-12$  per mil can be inferred. An appropriate mean solute composition of this water is not known, but sulphate should be at least as high as  $0.35 \text{ meq l}^{-1}$  (Figure 8) since values as high as this were recorded from the main meltstream at minimum flows. The discharge increased more than 20-fold between 24.00 h and 01.00 h at site A, yet at 01.00 h the shift in  $\delta^{18}\text{O}$  (Figure 8a) requires only 25 per cent rainwater input to this discharge. Given the minimal snow in the proglacial zone adjacent to A, this observation requires enhanced delivery of isotopically light snow- and icemelt water. Perhaps both proglacial runoff and a kinematic flood wave (as observed elsewhere by Nolan and Hill (1990) and on a smaller scale on a diurnal basis at Tsanfleuron) played a role in this enhanced delivery of water. Nevertheless, the increased solute concentration requires increased efficiency of delivery of ions from the subglacial zone. Evidence of a significant change in subglacial hydrology is that for a minimum of several days after the storm event, enhanced delivery of sulphate (scaled to discharge) by the main meltstream was observed (Figure 9), compared with the period before the storm event. Despite this, suspended sediment concentrations were not higher for a given discharge in the later period, except in the few hours after the storm. Also, by the middle of sampling period 4, the oxygen isotope values had fallen back to their original baseline in the early part of sampling period 2. Therefore the increased sulphate yields do not directly reflect rainwater input, but must reflect a rearrangement of the en-/subglacial drainage system forced by the high discharges resulting from rainfall. This had the effect of allowing increased drainage from low W/R ratio weathering environments, but without enhanced production of suspended sediment. Comparison with Figure 7b illustrates that the sulphate

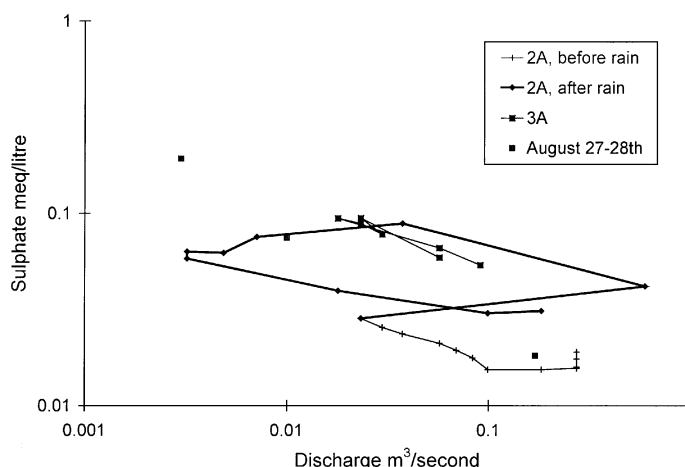


Figure 9. Cross-plot of sulphate versus discharge illustrating the higher sulphate concentrations at a given discharge in the period after the rainstorm in sample period 2 compared with the period beforehand

excess of the waters in the post-storm period was larger than the Sr excess, and that there was therefore increased delivery of more evolved 'old' waters to the main meltstream.

The greater proportional increase in nitrate than calcium or sulphate is a notable feature (Figures 6e and 8b). Comparison with periods of normal diurnal flows (e.g. sampling period 4, Figure 6) illustrates that this is far in excess of that expected from subglacial sources. The higher deviation from the baseflow–rainwater mixing line for nitrate than sulphate in relation to the composition of groundwater spring waters (cf. Figure 8a and b) implies that proglacial subsurface sources are also insufficient. The implication is that there are significant soluble nitrate reserves in soil zones, presumably organically derived. There is a contrast with vegetated environments where nitrogen inputs may exceed outputs during storms (Mulholland *et al.*, 1990). Organic sources of nitrogen should therefore be considered in catchment models of proglacial systems, and nitrogen and oxygen isotope analyses of nitrate provide a potential means of isolating mechanisms of nitrate formation (Kendall *et al.*, 1995a). Subglacial bacterial activity also needs to be considered.

### SOLUTE YIELDS

Calculations of total solute yields from glacierized drainage basins has attracted considerable interest (Anderson *et al.*, 1997), although there are difficulties posed by variations in water discharge and solute concentration on different time scales. Calculations of daily fluxes of ions from chemical analyses and discharge data clearly show the importance of the higher discharge flows, as has been demonstrated elsewhere (e.g. Wadham *et al.*, 1997). In sampling period 4 at station C, hourly Ca fluxes, calculated as the product of calcium concentration and discharge, sum to 3800 equivalents (eq) over the 24 h period, 90 per cent of which (3400 eq) was transported during the higher discharge period between 11.00 and 22.00 h (Table III).

Calcium yields also increase significantly downstream. For example during the interval 13.00–24.00 h in sampling period 2 (the time period unaffected by rain), Ca yields at site C (3600 eq) are much higher than at site A (2500 eq). Under normal conditions, discharges increase downstream by less than 10 per cent (the limit of error of discharge measurements) due to tributary input and bank seepage. The increase in Ca concentrations downflow is principally because of in-channel calcite dissolution. Figure 6b illustrates that Ca concentrations typically increase by 0.15 meq between stations A and C (from 0.4 to 0.55 meq l<sup>-1</sup>) in the period of higher flows when solute fluxes are greatest. In sampling period 4, Ca increased by 0.08–0.1 meq l<sup>-1</sup> during the 20 min flow period between stations B and C (Figure 9a), almost entirely due to suspended sediment dissolution since tributaries are absent in this reach. Total suspended sediment dissolution fluxes of

Table III. Calculated solute yields during study periods

Station/sampling period	Time period	Total discharge (m <sup>3</sup> )	Ca concentration (meq l <sup>-1</sup> )	Ca yield (eq)	SO <sub>4</sub> concentration (meq l <sup>-1</sup> )	SO <sub>4</sub> yield (eq)
A2	12 h (13.00–24.00)	6050	0.38–0.48	2500	0.015–0.028	100
C2	12 h (13.00–24.00)	6050 (min.)	0.57–0.69	3600	0.028–0.054	190
A2	1 h around 01.00	2200	0.50	1100	0.042	90
C2	1 h around 01.00	2200 (min.)	0.72	1600 (min.)	0.071	160 (min.)
C4	24 h	5800	0.60–0.95	3800	0.054–0.36	470
C4	12 h (11.00–22.00)	5200	0.60–0.95	3400	0.054–0.36	410

Ca between A and C will be around 50 per cent higher (i.e. 0.12–0.15 meq l<sup>-1</sup>) over the total 30 min travel time. Proportionally, therefore, the input of Ca from tributaries and bank seepage must be small. However, much higher proportional yields are expected from ions which are derived largely from low W/R ratio weathering because their concentrations are high in waters from tributaries and riverbank seeps. Sulphate is a simple example because it is not derived by weathering of suspended sediment during flow. Sulphate yields during the 12 h of higher flows at station A in sampling period 2 cumulate to 100 eq (Table I), compared to 190 eq at C (without allowing for increased discharge because of tributary input). Thus, in this case, the proglacial area delivered almost as much sulphate as drainage from the glacier, despite flow rates being more than an order of magnitude less. Nevertheless, the sulphate yields from sampling period 4 (station C), following reordering of the en-/subglacial drainage system after the storm of sampling period 2, were twice as high again (Table III).

The association of high solute yields with high discharges also applies during periods of rain. In sampling period 2 at station A, Ca flux (Table I) at 01.00 occurred at an hourly rate of 1100 eq (an hour is a minimum estimate of the duration of these flows). The flux at B is not known because of a lack of discharge data, but a minimum value is 1600 eq (using the Ca concentration at C and the discharge at A, that is neglecting the runoff entering the stream between A and C). Even this minimum estimate of total Ca flux out of the proglacial environment related to the storm is half the normal total daily flux.

The ultimate yields from the catchment will be slightly higher than those recorded in the study area, because streamwaters approaching the 1855–1860 terminal moraine are still undersaturated with calcite (Fairchild *et al.*, 1994a). However, subsequent dissolution of suspended sediment to reach saturation will increase ion yields by less than 10 per cent.

The annual ion yields cannot be estimated with confidence because there are no measurements of the ion contents or expected discharges in the early melt season, but this is a fault of most other previous studies too. Ion yields in both glacial and non-glacial systems are strongly controlled by total runoff (Sharp *et al.*, 1995a; Bluth and Kump, 1994; Anderson *et al.*, 1997). However, a minimum figure is given by assuming 100 days of discharge at August rates. Also, since Anderson *et al.* (1997) stress the important control of specific discharge (cubic metres of water per square metre catchment area per year) on cation yields, some preliminary comparisons with other glaciated basins can be made, although only in a few cases are data truly representative of a melt season. Given 100 days of discharge at 5800 m<sup>3</sup> per day (as observed in sampling period 4) and an estimated drainage area of 3 km<sup>2</sup>, an annual specific discharge can be computed of 0.22 m per year. This figure appears to be very low given that much higher rates of precipitation occur at lower altitudes: extensive loss of water into karst underlying glacial and proglacial sediments can be inferred (Figure 2). We make the conservative estimate that average daily fine weather calcium yields of around 3800 eq are increased by 10 per cent to 4200 eq by a combination of calcite dissolution to reach saturation and the effects of periodic rains. This equates to total cation yields of around 5600 eq per day approximately equivalent to 3.9 t km<sup>-2</sup> per year. This can be expressed as a yield of 17 ton per km<sup>2</sup> catchment per m specific

runoff which compares with values between 5 and 10 in other glacial catchments summarized by Anderson *et al.* (1997). This high value is plausible because of the soluble nature of the carbonate bedrock at Tsanfleuron compared with the predominantly silicate terrains summarized by Anderson *et al.* (1997).

A factor missing in most studies is the exchangeable ion load. Souchez and Lemmens (1987) stress the role of ion exchange reactions, but only Eyles *et al.* (1982) have determined exchangeable ions in the context of a study on ion loads. The exchangeable ion load is likely to be significant where clay minerals are abundant.

Further understanding of the comparative effectiveness of proglacial and glacier-covered alpine environments in delivering solutes in this environment would require information on:

- (1) the increase in precipitation with altitude on the glacier-covered part of the catchment;
- (2) discharge and solute load of the main meltstream in both early and late melt seasons;
- (3) comparative discharge and solute yields of proglacial snowmelt streams in the early summer with minor tributary flows and episodic rain-induced overland flows in the late summer.

Present indications of the relative efficiency of proglacial and glacier-covered parts of the catchment, a theme introduced by Axtmann and Stallard (1995), are as follows. Although summer rains can be effective in mobilizing solutes, the relative proportions derived from subglacial and proglacial sources are not clear. Recharge of rainwater from rainstorms is implied by the isotopically heavy composition of spring water. Although combination of seepage and tributary flow efficiently delivers solutes at low discharge in the proglacial environment, snowmelt streams on valley sides were observed to bear very low solute loads, presumably because of their low efficiency in interacting with the bed. Thus the melting of winter precipitation may be less efficient at yielding solutes than summer rain, a hypothesis that clearly requires testing. The subglacial environment (Figure 2) is able to create highly energetic flow conditions by which water, suspended sediments and water seeping from low W/R ratio weathering environments are able to interact effectively diurnally, if not continuously. Under such conditions, rapid flushing of turbulent meltwaters with significant suspended sediment concentrations leads to efficient generation of solutes (Sharp *et al.*, 1995b), a process that also applies to sediment-laden waters in the proglacial environment. Our study has also indicated the possibility of revitalizing the ability of the subglacial drainage system to generate solutes by summer rainfall events.

## CONCLUSIONS

- (1) Stable isotope studies reveal that tributary and bulk meltstream waters, and rain and most glacier ice samples lie on a single meteoric water line ( $\delta D = 8.3 \delta^{18}O + 14$ ). Bulk meltwaters in the study period have an oxygen isotope compositional baseline of around  $-12$  per mil without diurnal variations. The bulk meltstream compositions become significantly heavier following periods of rain.
- (2) The atmosphere is the primary source of nitrate, chloride and sodium. Nitrate is enhanced in the water emanating from the subglacial distributed flow system suggesting that this system is recharged by early season snowmelt.
- (3) Rapid dissolution of calcite in contact with pure meltwaters leads to water compositions of  $0.3\text{--}0.45$  meq  $\text{l}^{-1}$  Ca and low ratios of other ions to Ca. Glacial meltwater approaches this composition at peak discharge.
- (4) Low water/rock ratio weathering of glacial debris leads to high Mg, Sr and  $\text{SO}_4$  concentrations (also high Na and K in the northern part of the catchment) as a result of non-congruent dissolution of calcite, oxidation of pyrite and minor dissolution of aragonite and weathering of silicates. Although non-congruent calcite dissolution leads rapidly to characteristically high Mg/Ca and Sr/Ca, waters with such compositions are always found with enhanced sulphate because water flow through low water/rock ratio weathering environments is always slow. Minimum-flow waters in the main meltstream display such characteristics.

- (5) Under dry weather conditions, meltwaters at the glacier snout are modified appreciably as they flow downstream in the proglacial zone by input of ions from tributary input and bank seepage, together with congruent dissolution of calcite present as suspended sediment.
- (6) Rainstorm events lead to increased rather than decreased solute concentrations, and generate substantial increases in solute fluxes. Nitrate fluxes increased most, which may be because of generation of nitrate in soil zones of the proglacial environment. The system is too complex to produce an adequate hydrographic separation, but a two-component mixture of existing baseflow and rainwater is clearly inadequate. The effect of one significant rainstorm was to perturb the subglacial drainage system, leading to higher solute fluxes per unit discharge in at least the following week.
- (7) Solute yields from the basin are estimated to be unusually high for glacial systems (17 ton per km<sup>2</sup> catchment per m specific runoff) because of the reactivity of the impure carbonate sediments. Errors in calculating yields stem from a lack of knowledge of total water fluxes, and uncertainties as to the area over which meltwater is lost to the underlying karstic system.
- (8) Unvegetated proglacial environments are effective at yielding solutes during the summer period (although less so than lower latitude environments), but it is hypothesized that spring snowmelt may be less effective at yielding solutes in the proglacial environment than if passed through a glacier, because of their less efficient introduction into low W/R ratio weathering environments.

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